Defense Technical Information Center Compilation Part Notice

ADP017728

TITLE: Destruction of Nitrocellulose Using Alkaline Hydrolysis

DISTRIBUTION: Approved for public release, distribution unlimited

Availability: Document partially illegible.

This paper is part of the following report:

TITLE: Proceedings of the Tri-Service Environmental Technology Workshop, "Enhancing Readiness Through Environmental Quality Technology" Held in Hershey, PA on 20-22 May 1996

To order the complete compilation report, use: ADA429790

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP017697 thru ADP017729

DESTRUCTION OF NITROCELLULOSE USING ALKALINE HYDROLYSIS

Tsan-Liang Su and Christos Christodoulatos
Center for Environmental Engineering
Stevens Institute of Technology
Hoboken, NJ 07030

ABSTRACT

Due to demilitarization activities in the United States, large amounts of energetic materials which have been accumulated over the years in various manufacturing and military installations, have to be dealt with in an environmentally acceptable manner. Historically, the method of choice for destruction of energetic materials has been open burning or open detonation which are neither safe nor environmentally desirable. Alkaline hydrolysis appears to be a simple, inexpensive method for breaking explosives and propellants down to non-energetic materials that can be directly disposed or further treated biologically. Nitrocellulose is one of the energetic materials classified as reactive (40 CFR § 261.21) and is listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste. This study focused on the kinetics of decomposition of nitrocellulose using sodium hydroxide at different dosage levels, temperature, and contact times. Significant levels of denitration and breakdown of the backbone of cellulose structure were achieved by this method. The post-digestion products consist of organic and inorganic substances with sodium nitrite and nitrate being the major nitrogen containing compounds. The ratio of nitrite-N to nitrate-N is slightly changed at different sodium hydroxide concentrations but it approaches a value of 3 regardless of the degree of digestion. The time required for complete destruction varies with concentration of sodium hydroxide and temperature. Kinetic modeling showed that the process follows a pseudo-first-order rate law. The present work indicates that alkaline digestion may be the technology of choice for the destruction of nitrocellulose in various gun and rocket propellants, and for the treatment of nitrocellulose laden effluents from munitions manufacturing facilities.

INTRODUCTION

In demilitarization activities, Environmentally acceptable degradation of associated with energetic material waste to non-energetic forms is a critical objective. Large amounts of energetic materials which have been accumulated over the years in various manufacturing and military installations, have to be dealt with in an environmentally acceptable manner. Historically, the method of choice for destruction of energetic materials has been open burning or open detonation which are neither safe nor environmentally desirable

Cellulose nitrate, also more commonly called nitrocellulose shown in Figure 1, is one of the important derivatives and has been widely used as wood finish, ink bases, filter membranes and explosives. High nitrogen content Nitrocellulose, a principal energetic ingredient of propellants, has been classified as reactive (40 CFR § 261.21) and is listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste.

Various physicochemical and biological processes have been developed for the removal of nitrocellulose and nitrocellulose fines in industrial process wastewater. These removal processes classified as a physicochemical mean include microfiltration, coagulation, sedimentation, air floatation, and alkaline or acid hydrolysis.[1-5] It is also well documented in the literature that nitrocellulose was resistant to direct biodegradation under either aerobic or anaerobic conditions.[5-9] Therefore, among the various processes, alkaline hydrolysis appears to be a simple, inexpensive method for breaking nitrocellulose down to non-energetic materials that can be directly disposed or further treated biologically.

Kenyon and Grey[1] reported the presence of a wide variety of organic and inorganic products resulting from the alkaline hydrolysis of nitrocellulose such as nitrates, nitrites ammonia, cyanide, malic, oxalic, glycolic, trioxyglutaric, dioxybutyric, malonic, tartonic and other unidentified complex acid, sugar, modified cellulose and their nitrates, and partially denitrated cellulose nitrate. Edge et al.[10] suggested two possible degradation pathways, shown in the Figure 2, which were based on the formation of nitrites and nitrates by the action of alkali on nitrocellulose. One of these is simple ester hydrolysis where any acid formed would be neutralized by degrading base and hence any degradation nullified. The other possible mechanism could result in the production of carbonyl groups forming an oxidized cellulose.
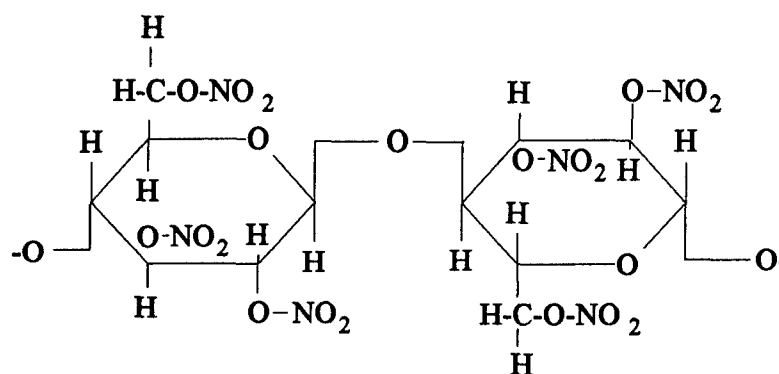

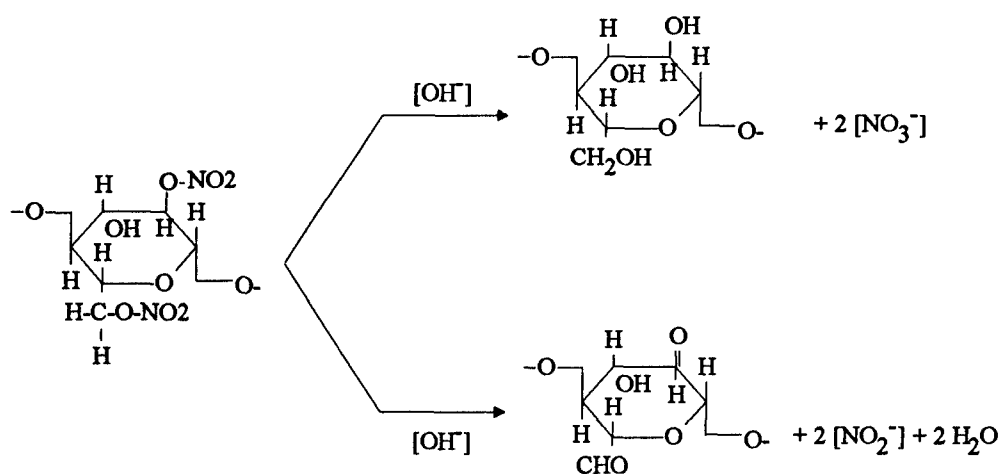Figure 1: Chemical structure of fully nitrated nitrocellulose

Figure 2: Two Possible Mechanisms of Nitrocellulose Hydrolysis by Alkaline Attack

338

Quantitative studies of this reaction are more or less fragmentary. The formation of nitrites and nitrates by the action of alkaline hydrolysis of nitrocellulose has been quantitatively measured[1, 4, 7]. Various authors have also studied in a quantitative manner the effect of certain variables such as the type of bases, concentration of alkaline solution, temperature, and time[1, 7].

Unfortunately, there was no extended studies of the kinetics of decomposition of nitrocellulose by alkaline hydrolysis. Therefore, the purpose of this study is to establish the relationship between nitrocellulose and base solution, by the application of simple analytical methods at each step of the degradation process.

As for nitrocellulose hydrolysis, the literature provides inadequate data on kinetics. This may be resulted from lack of a simple and accurate analytical method to measure nitrocellulose directly. With regard to this, the literature reports several methods to determine directly or indirectly unutilized nitrocellulose to ensure nitrocellulose quality in chemical and biological processes[3, 11] On the present studies, total suspended solid (TSS), the most common method at the plant, was measured and to assume that all TSS was nitrocellulose. Nitrates and nitrites released by alkaline hydrolysis was also monitored to compute nitrogen content and determine nitrocellulose concentration indirectly.

MATERIALS AND METHODS

Several alkaline hydrolysis tests were successively conducted during this investigation. Nitrocellulose was provided by Aqualon, a division of Hercules Incorporated (Wilmington, DE), with approximately 12.2% nitrogen content.

Various doses of sodium hydroxide were used to evaluate the degradation rate of nitrocellulose. Sodium hydroxide solutions were prepared with 0.2%, 0.5%, 1.0%, and 2.0% by weight and were preheated in a water bath prior to their introduction in the reactor. The experiments were carried out in a batch reactor equipped with a mixer and a precision auto temperature controller (Parr Instrument Company, Moline, IL). The experimental set-up is shown schematically in Figure 3.
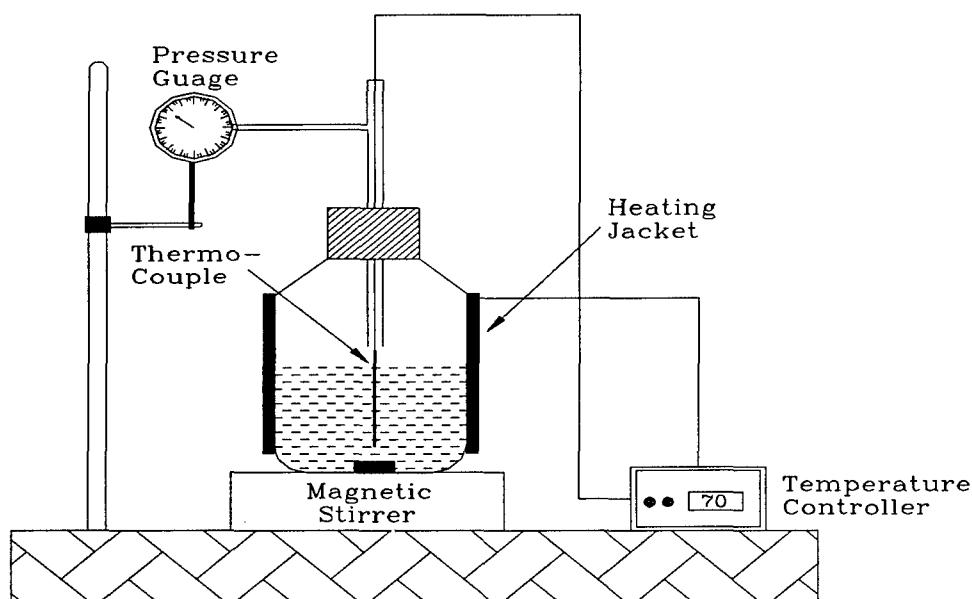

Figure 3: Batch Reactor for Nitrocellulose Hydrolysis

In each batch experiment, approximately 1 gram of nitrocellulose was introduce to the reactor with certain concentration of sodium hydroxide at 70 °C. Concentrations of nitrate, nitrite, and sodium hydroxide and residual of nitrocellulose were monitored every 5 minutes for up to 35 minutes of reaction time. When the time was up at each reaction period, the reactor along with sample were transfer to ice bath to quickly bring temperature down to room temperature. The reactor contents were collected and filtered through a crucible equipped with Whatman 934-AH glass microfiber filter (Whatman Inc., Clifton, NJ) to determine TSS as nitrocellulose residual. Filtrate was collected and nitrate and nitrite concentration were determined by direct injection of filtrate using High Performance Liquid Chromatography (HPLC) on a Varian LC Workstation (Varian, Sugar Land, TX) equipped with a diode array detector, and a Durasep A-1 4.6 mm x 100 mm, 5μm (Alltech Associates Inc., Deerfield, IL) Chromatographic column..

RESULTS AND DISCUSSIONS

Nitrocellulose (NC) decomposition was studied at 70 °C with varying alkali to nitrocellulose ratio. The degree of digestion and the concentrations of nitrite and nitrate were monitored for 35 minutes reaction time at each 5-minute time interval. Typical results of NC hydrolysis are illustrated in Figure 4. Pure NC appears to degrade faster at 2% of NaOH concentration than at 1% or less of NaOH dose. Moreover, 90% of NC digestion was achieved at 2% NaOH dose within 35 minutes. Figure 5 and 6 present nitrate and nitrite nitrogen released during nitrocellulose decomposition. The ratio of nitrite-N to nitrate-N is approximate 2.97 regardless of the degree of digestion. This finding is in good agreement with the results obtained by Kenyon and Gray[1] who found 0.075 mole of nitrite and 0.025 mole of nitrate per liter of alkaline decomposition mixture. Moreover, the independence of this ratio from the degree of digestion suggests that the hydrolysis of nitrocellulose is a single step process where nitrates and nitrites are formed directly from the cleavage of the parent molecules. Wendt and Kaplan[7] also demonstrated that the decomposition of NC in alkaline environments proceeds in a single step, by determination of the nitrogen, carbon and oxygen contained in the residual (undigested) NC during the course of the reaction.
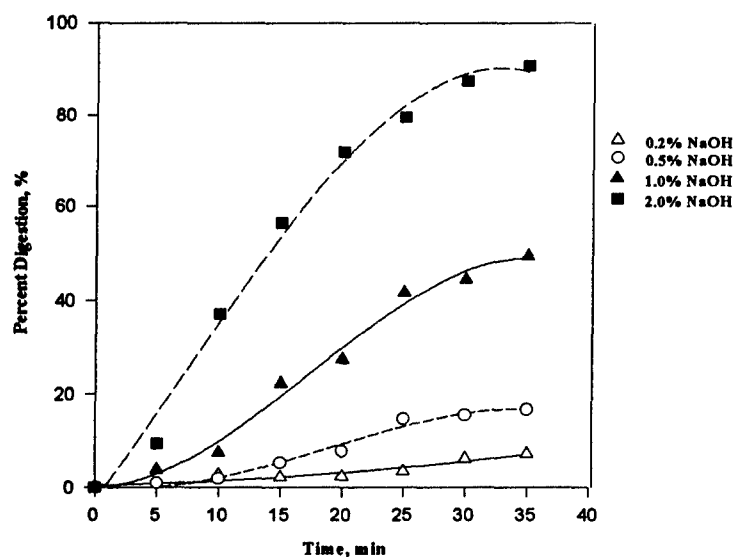

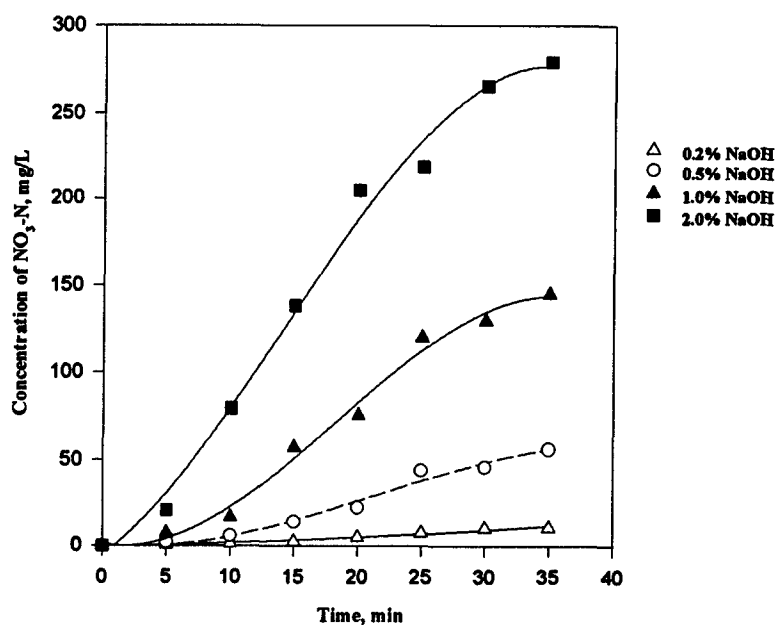Figure 4: Nitrocellulose Decomposition with Various Sodium Hydroxide Strength

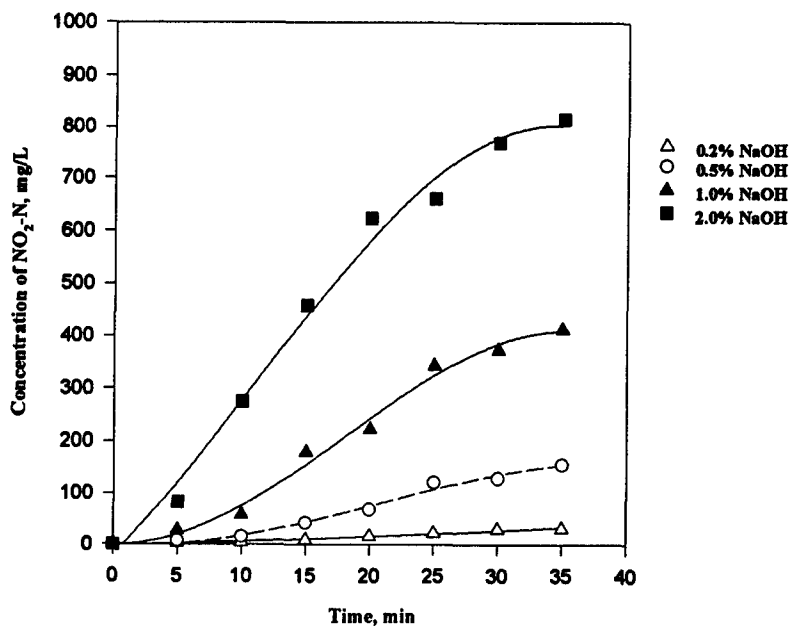Figure 5: Nitrate-nitrogen Released during NC Decomposition

Figure 6: Nitrite-nitrogen Released during NC Decomposition

Preliminary kinetic analysis indicated that the concentration-time history of NC decomposition can be accurately described by a pseudo-first order rate law of the form:

$$\frac{dC}{dt} = -kC$$

where C is the nitrocellulose concentration and k is the first order rate constant. However, the first order rate constant k is a function of NaOH concentration and additional data are required in order to establish its dependence on NaOH concentration.

CONCLUSIONS

The results obtained from this study indicate that alkaline hydrolysis is a viable method for the destruction of nitrocellulose. Alkaline decomposition can be described by a pseudo first order kinetic law but the dependence of the rate constant on the concentration of the alkali must be established at the desired temperature. Nitrogen released during the alkaline digestion is mainly in the form of nitrite and nitrate. The observed ratio of nitrite-N to nitrate-N was approximately 3 and it was independent of the degree of digestion or NaOH concentration.

ACKNOWLEDGMENT

REFERENCES

1. Kenyon, W. O., and Gray, H. LeB., "The Alkaline Decomposition of Cellulose Nitrate. I. Quantitative Studies." *Amer. Chem. Soc. Jour.*, 8, 1422 (1936).

2. Spontarelli, T., Buntain, G. A., Sanchez, J. A., and Benziger, T. M., "Destruction of Waste Energetic Materials Using Base Hydrolysis."

3. Kim, B. J., and Park, J. K., "Comprehensive Evaluation and Development of Treatment Technologies for Nitrocellulose Fines in Process Wastewater." Nitrocellulose Fines Separation and Treatment Workshop Proceedings, West Lafayette, IN, 1 (1993).

4. Alleman, J. E., Kim, B. J., Quivey, D. M., and Equihua, L. O., "Alkaline Hydrolysis of Munition-Grade Nitrocellulose." Nitrocellulose Fines Separation and Treatment Workshop Proceedings, West Lafayette, IN, 50 (1993).

5. Hsieh, H.-N.,and Tai, F.-J., "Anaerobic Digestion and Acid Hydrolysis of Nitrocellulose." Nitrocellulose Fines Separation and Treatment Workshop Proceedings, West Lafayette, IN, 110 (1993).

6. Brodman, B. W., and Devine, M. P., "Microbial Attack of Nitrocellulose." *J. Appl. Polym. Sci.*, 26, 997 (1981).

7. Wendt, T. M., and Kaplan, A. M., "A Chemical-Biological Treatment Process for Cellulose Nitrate Disposal." *J. Water Pollut. Control Fed.* 48, 660 (1976).

8. Gallo, B., Allen, A., Bagalawis, R. L., Woodbury, C., Yang, A., Austin, P., and Chaplain, D., "Microbial Degradation of Nitrocellulose." Nitrocellulose Fines Separation and Treatment Workshop Proceedings, West Lafayette, IN, 78 (1993).

9. Duran, M., Kim, B. J., and Speece R. E., "Anaerobic Biotransformation of Nitrocellulose." *Waste Management*, 14, 481 (1994).

10. Edge, M., Allen, N. S., Hayes, M., Riley, P. N. K., Horie, C. V., and Luc-Gardette, J., "Mechanisms of Deterioration in Cellulose Nitrate Base Archival Cinematograph Film." *Eur. Polym. J.,* **26**, 623 (1990).

11. Sharma, A., Sundaram, S. T., Zhang, Y.-Z., and Brodman, B. W., "Biodegradation of Nitrate Esters. 2. Degradation of Nitrocellulose by a Fungus Isolated from a Double-Base Propellant." *J. Appl. Polym. Sci.,* **55**, 1847 (1995).